SECTION 7

SAMPLING AND ANALYSIS

7.1 General Discussion

This section is intended to address USTs which contain petroleum only. Guidance on USTs containing hazardous substances may be obtained from DOH. In several cases, as listed below, UST owners and operators are required to measure for the presence of a release (e.g., collecting and analyzing soil and water samples) at UST sites:

- For a site assessment as required while conducting investigations of suspected releases (HAR 11-281-63(b)(2);
- For a site assessment as required while conducting permanent UST closure or change-in-service (HAR 11-281-83);
- For soil and/or water investigations as required while conducting release response activities (HAR 11-281, Subchapter 7); and
- For soil, water, and/or air monitoring as required in determining the progress and efficiency of site cleanliness.

UST owners and operators and their consultants/contractors engaged in these activities should find the following detailed technical guidance useful in planning for and conducting their work. Adherence to these guidelines is critically important to making responsible cleanup decisions and to ensure that these measurements are defensible in a court of law.

The evolution of environmental data requirements over the years has been significantly driven by legal concerns. Regulatory agencies have had to provide more reliable, defendable data to their attorneys in order to enhance the likelihood of successful enforcement actions. The corporate and private sectors similarly require better environmental data for their legal protection, financial decision-making, and liability control. Lending institutions, real estate developers, and insurers require good environmental data to assess financial risks and to minimize future liabilities. The degree of reliability desired from environmental data may vary, depending on the case at hand.

Consequently, UST owners and operators and their consultants/contractors must exercise prudent judgment and wise decision-making in procuring the appropriate level of data for reliable site-specific environmental data needs.

The level of reliability in data obtained and work performed for a particular UST activity is directly related to the level of confidence desired for that activity. This level of confidence is determined by the data quality objective (DQO), which is determined largely by the nature of the specific environmental problem at hand and liability-related factors. For the technically-oriented user of this manual, a brief primer on data quality objectives is provided in Appendix 7-A.

For the UST program, there are three levels of data quality, and these levels and their uses are tabulated in Appendix 7-A. Unfortunately, the cost of environmental data tends to rise dramatically as the desire for precision becomes greater. This is mostly a function of quality assurance/quality control measures and of analytical costs. In general, field measurement methods, which have limited reliability and reproducibility, are relatively inexpensive. Conversely, laboratory analytical measurement methods are highly reliable but can be very costly. Both types of measurement methods are, of course, only as reliable as the sample collection methods employed. However, there may be opportunities to economize as some interim phases of release response work may not warrant a high reliability in data. For these types of work, one should seriously consider the use of field measurement methods instead of prescribed analytical laboratory methods to obtain data to suit the purpose intended.

If alternate, more economical measurement methods can be used to appropriately scope or screen for contaminant presence, then DOH encourages their use for that purpose. As a result, considerable cost savings may be realized for the owner and operator. The U.S. EPA document tiltled *Expedited Site Assessment Tools for Underground Storage Tank Sites A Guide for Regulators* (EPA 510-B-97-001), dated March 1997, is an excellent reference which describes various site assessment tools including field analytical methods

for petroleum hydrocarbons. This document is useful for evaluating expedited site assessment tools (e.g., surface geophysical method, soil-gas survays, direct push technologies, field methods for hydrocarbon analysis) which may be appropriate for a particular release investigation.

DOH suggests that, if possible, the owner and operator reserve costly laboratory analyses for activities that require high reliability data. These include, but are not limited to, data to verify residual contaminant levels, risk assessment data, remedial design data, and potentially controversial cases where litigation may be likely, involving government or private parties.

7.2 Sampling and Analysis Planning

There is no substitute for good project planning. This is critical especially for the owner and operator who wishes to develop or improve a site but must first deal with USTs found at the site. One should plan for activities wisely by building into the schedule ample time for environmental contingencies. This is particularly important for sites that may have had previous commercial/industrial activities. A thorough records search of the past use of a site up front can often translate into cost savings for UST owners and operators, especially when it comes to selecting sampling locations, sampling and analysis costs, and confident decision-making based on environmental data.

Under ideal circumstances, all sampling investigations conducted at a UST site should be conducted in accordance with a Quality Assurance Project Plan (QAPP). Any UST consultant/contractor who performs sample collection and analysis should have a generic QAPP (e.g., applicable to all sites for all levels of data procurement) to ensure that the data obtained from even the simplest sampling event is reliable for its intended purposes. A QAPP describes the policy, organization, functional activities and quality assurance/quality control protocols necessary to achieve one or more data quality objectives dictated by the intended use of the data. The QAPP includes, among other

things, field quality assurance/quality control measures, laboratory quality control requirements, data validation procedures, and performance audit procedures. For very complex sites or for exceptionally detailed investigations, it may be appropriate to prepare a site-specific QAPP. The consultant/contractor should be able to determine if a separate QAPP is necessary. In the event the consultant/contractor wishes or needs to prepare a QAPP, a suggested outline is provided for reference as Appendix 7-B.

The Sampling and Analysis Plan (SAP) consists of the QAPP and a Field Sampling Plan (FSP). The FSP defines in detail the sampling and data gathering activities to be used at a specific site. The purpose of a site-specific SAP is to ensure that sample data collection activities will be comparable to and compatible with previous data collection activities performed at the site while providing a mechanism for planning and approving field activities. The SAP is an integral part of a data report and should be made part of the final data report package in support of findings and conclusions. An outline of a site-specific Field Sampling Plan is provided in Appendix 7-C.

It is important to point out that the State UST regulations do not specifically require UST owners and operators to develop and submit a Sampling and Analysis Plan prior to sampling activities at a UST site. Further, DOH does not intend to require UST owners and operators to specifically submit SAPs, QAPPs, or FSPs prior to a sampling activity. However, because these plans are vitally important to documenting the reliability of any sampling data generated from a UST site, DOH encourages their inclusion as part of the final data report package for the site work. In addition, these plans and the final data report package should be kept as part of UST owners and operators records.

Expedited site assessment (ESA) is a framework for **rapidly** characterizing underground storage tank conditions for input to corrective action decisions. ESAs have been made possible in recent years by the development of improved, cost-effective methods for rapid collection and field analysis of soil, soil-gas, and groundwater samples. The ESA process

contrasts with conventional site assessments in which a significant amount of analysis and data interpretation is completed offsite at a later date. The DOH has adopted a Risk-Based Corrective Action (RBCA) process for sites with contaminated soil and groundwater. ESA's can be integrated with RBCA evaluations because the ESA process is a method of obtaining accurate site information that is necessary for making an appropriate corrective action decision. The first two RBCA tiers can be evaluated in a single mobilization as part of a standard ESA. The data needs for Tier 3 evaluation can also be aquired in the same mobilization; however, because of the complexity and cost of the data needed for this level of evaluation, investigators must be prepared for this tier level prior to mobilization. Owners and operators must decide whether the ESA is more appropriate for their site than the conventional site assessment approach.

The ESA process is described in detail in the U.S. EPA document titled *Expedited Site Assessment Tools for Underground Storage Tanks A Guide for Regulators*, EPA 510-B-97-001, dated March 1997.

7.3 Sample Control

Reliability of environmental data depends not only on the methods of sample collection and analysis, but also on maintaining the integrity of the sample during handling and transport. All samples collected from a UST site should be controlled from the point of collection to the analytical laboratory and eventually to the analytical chemist who analyzes the samples. Details of sample control procedures are presented in Appendix 7-D. At a minimum, all collected samples should be:

1. Properly identified using sample ID labels/tags; and
2. Properly contained, preserved, and transmitted from the point of collection to the analytical laboratory with an unbroken chain-of-custody.

This kind of documentation provides adequate sample control that further ensures the reliability and defensibility of sample data obtained.

7.4 Sample Collection Procedures

The importance of using good sampling methods or procedures cannot be overstated. Good data depends on good field practice and procedure. UST owners and operators and their consultants/contractors must employ sample collection procedures and sampling personnel that can ensure that representative samples are collected. UST owners and operators and their consultant/contractors must also ensure that sample handling does not result in cross-contamination or unnecessary loss of contaminants. Since gasoline and some of the other petroleum products consist largely of volatile organic compounds, special care in sample collection is required due to the high potential for loss of these volatile compounds from the sample. The sampling methods and equipment used will always depend on the site-specific conditions. Good professional judgement and experience on the part of UST consultants/contractors are necessary in determining which sampling procedures are appropriate for a particular site. DOH's recommended procedures for soil and water sampling are presented in Appendix 7-E.

When conducting site investigation work, the use of field instruments and methods is recommended to help screen for extent of a release at contaminated areas. In fact, this screening or scoping exercise should be included as part of the SAP. Field instruments and methods are also useful for monitoring potential exposures to workers and determining appropriate health and safety precautions. UST owners and operators and UST consultants/contractors should see Appendix 7-F for a general discussion on the use of field instruments.

Although field instruments and methods described in Appendix 7-F can be used successfully to measure for the presence of specific contaminants, they all have their limitations. Excessive reliance on field instruments and methods can result in incorrect conclusions, or conclusions that are difficult to verify without performing subsequent laboratory analysis. More information and discussion on field measurement methods can be found in the EPA document entitled "Field Measurements - Dependable Data When You Need It," EPA/530/UST-90/003 (September 1990).

7.5 Recommended Analytical Methods for Soil and Water

For UST closures and release response, DOH's recommended sample preparation and analytical methods for analyzing soil and water samples are listed in Table 7.1. DOH's recommended chemical analysis for UST closures and release response are shown in Table 7.2. While other methods are not prohibited, the use of other methods may substantially delay DOH's data review process by requiring additional evaluation of the applicability and appropriateness of the methods used.

The analytical methods selected to obtain soil and water data must be compatible with the type of substances stored in the UST over its lifetime and any other contaminants that may be present at the site because of past commercial/industrial activities. Choosing methods to identify and quantify petroleum contamination in the environment can be difficult, because petroleum products are complex mixtures consisting of several hundred different hydrocarbon compounds. Therefore, the practical approach is to use methods that analyze for certain indicator compounds or classes of compounds with similar characteristics. One of the most important characteristics of some petroleum products is volatility or the tendency of a compound to evaporate. For example, certain petroleum products, like gasoline, are highly volatile and can be conveniently measured by five indicator volatile organic constituents: benzene, toluene, ethylbenzene, and xylene (BTEX) and methyl teriary-butyl ether (MtBE). Any volatile constituents of gasoline can be grossly quantified by measuring total petroleum hydrocarbons (TPH) as gasoline. Petroleum products such as diesel and fuel oil contain much less volatile compounds than gasoline, and the semi-volatile and non-volatile constituents of these petroleum products can be grossly quantified as TPH as diesel. For these products, measurement for BTEX is also recommended to address the volatile component of these products, albeit minimal.

Table 7.1 Recommended Sample Preparation and Analytical Methods

The following are methods recommended by the Solid and Hazardous Waste Branch's Underground Storage Tank Section for preparing and analyzing soil and water samples. The use of alternative methods is not prohibited, however, the use of other methods should receive the approval from DOH prior to their use to ensure their acceptability for their intended use.

Analytes	Soil	Water	Primary Equipment	Sample[1] Preparation
TPHs	4030[2]		Immunoassay	Included in kit
Polynuclear Aromatic Hydrocarbons (PAHs)	4035[2]		Innmunoassay	Included in Kit
Polynuclear Aromatic Hydrocarbons (PAHs) Acenaphthene, Naphthalene, Fluoranthene, Benzo(a)pyrene	8100[3]	8100	GC/FID	Extraction
	8310	8310	HPLC/UV Flourescence	Extraction
	8270B[4]	8270B	GC/MS	Extraction
TPH as Gasoline	8015B[5]	8015B	GC/FID	Purge-and-Trap and Headspace
	8015 Modified	8015 Modified[6]	GC/FID	Purge-and-Trap
TPH as Diesel	8015B	8015B	GC/FID	Extraction
	8015 Modified	8015 Modified	GC/FID	Extraction
Oil and Grease	9071A[7]		Oil and Grease Extraction Method for Sludge and Sediment Samples	Extraction
		9070[8]	Gravimetric Separatory Funnel Extraction	Extraction/Evaporation
	8015 Modified	8015 Modified	GC/FID	Purge-and-Trap
Total Recoverable Petroleum Hydrocarbons (TRPH)	8440[9]	-	IR Spectrophotometer	Supercritical Fluid Extraction from Soils
	-	418.1[10]	IR Spectrophotometer	Extraction
Benzene, Toluene, Ethylbenzene, Xylene (BTEX)	8015B	8015B	GC/FID	Purge-and-Trap
	8021B[11]	8021B	GC/PID	Purge-and-Trap
	8260B[12]	8260B	GC/MS	Purge-and-Trap

Table 7.1 Recommended Sample Preparation and Analytical Methods

Analytes	Soil	Water	Primary Equipment	Sample[1] Preparation
Methyl Tertiary-Butyl Ether (MTBE)	8021B	8021B	GC/PID	Purge-and-Trap
	8260B	8260B	GC/MS	Purge-and-Trap
Halogenated Volatile Organics	8021B[13]	8021B	GC/ELCD	Purge-and-Trap
	8260B[12]	8260B	GC/MS	Purge-and-Trap
Polychlorinated Biphenyls (PCBs)	8082[14]	8082	GC/ECD	Extraction
Lead	7120	7120	Atomic Absorption, Direct Aspiration	Acid Digestion
	7421	7421	Atomic Absorption, Furnace Technique	Acid Digestion
	6010B	6010B[15]	Inductively Coupled Plasma-Atomic Emission Spectrometry	Acid Digestion
Cadmium	7130	7130	Atomic Absorption, Direct Aspiration	Acid Digestion
	7131	7131	Atomic Absorption, Furnace Technique	Acid Digestion
	6010B[15]	6010B	Inductively Coupled Plasma-Atomic Emission Spectrometry	Acid Digestion

[1] See Chapter 4 of SW-846 Update III for specific appropriate sample preparation methods.
[2] Screening methods for soils.
[3] 4-digit methods "Test methods for Evaluating Solid Waste", SW-846 Third Edition Final Updates, Revised May 1997.
[4] 8270B has replaced 8270.
[5] EPA Method 8015B has replaced EPA Method 8015. EPA Method 8015B now includes gasoline and diesel analyses.
[6] LUFT Methods - "Leaking Underground Fuel Tank Field Manual," California State Water Resources Control Board.
[7] EPA Method 413.2 and "Standard Method for the Examination of Water and Wastewater" APHA, AWWA, WPCF, 17th ed. (1989) Method 5520 C is equivalent to EPA Method 9071A.
[8] EPA Method 413.1 and "Standard Method for the Examination of Water and Wastewater" APHA, AWWA, WPCF, 17th ed. (1989) Method 5520 B is equivalent to EPA Method 9070.
[9] This method is similar to EPA Method 418.1, however, perchlorethane (PCE) is used as an IR solvent instead of Freon-113.
[10] EPA Method 418.1 - "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020.
[11] EPA Method 8020 has been replaced by EPA Method 8021B. The DOH recommends use of EPA Method 8021B but will allow continued use of EPA Method 8020 as an interim option.
[12] EPA Method 8240 has been replaced by EPA Method 8260B.
[13] EPA Method 8010 has been replaced by EPA Method 8021B. The DOH recommends use of EPA Method 8021B but will allow continued use of EPA Method 8010 as an interim option.
[14] EPA Method 8082 replaces EPA Method 8080.
[15] EPA Method 6010B replaces EPA Method 6010.

Table 7.2 Recommended Chemical Analysis for UST Closure and Release Response

The Solid and Hazardous Waste Branch's Underground Storage Tank Section recommends the following chemical analysis for soil and water samples. Refer to Table 7.1 for addtional information regarding sample preparation and analysis methodology.

SOURCE COMPOUND									
Unleaded gasoline	Leaded gasoline	Diesel	Jet Fuel	Kerosene	Fuel Oil	Waste Oil	Unknown	ANALYTICAL CONSTITUENTS	SITE ACTIVITY
X	X						X	TPH as Gasoline	Closure
		X	X	X	X		X	TPH as Diesel	
						X	X	TPH as Oil and Grease	
X	X	X	X	X	X		X	Benzene, Toluene, Ethylbenzene, (BTE)	Release Response
X	X						X	Methyl tert-Butyl Ether (MTBE)	
		X	X	X	X	X	X	Acenaphthene, Naphthalene, Fluoranthene	
		X	X	X	X	X	X	Benzo(a)pyrene	
						X	X	Halogenated Volatile Organics	
	X					X	X	Total Lead	
						X	X	Total Cadmium	
						X	X	Polychlorinated biphenyls	

An UST's site history frequently suggests past use, storage, or disposal of other substances in addition to petroleum fuel products in UST's. For instance, waste oil is commonly stored at UST sites, such as at garages and filling stations. Similarly, cleaning fluids, solvents, and various other chemicals may be present at UST sites depending on past chemical usage and practices on the property. Handling or storage and use of these chemicals necessitates testing for hazardous substances, such as halogenated (especially chlorinated) hydrocarbons and specific metals which may not even be related to a UST at the site. Confirmation of their presence may dictate additional regulatory requirements for cleaning up hazardous substance releases and perhaps regulations for handling, treating, storage and disposal of hazardous wastes. Releases from petroleum UST's are categorically excluded from RCRA hazardous waste regulations at this time except for sludge and sediment from the UST itself and contaminated soil and water attributed to a UST which fails for toxicity characteristic leaching process (TCLP) for metals. Nevertheless, even if these wastes are not hazardous wastes by definition, such wastes must nevertheless be handled carefully. As an example, tetraethyl lead (TEL) was once added to gasoline as an antiknock agent. TEL is a toxic substance and contaminated materials containing TEL should be handled in an appropriate manner, even though they are not defined as hazardous wastes. When appropriate, UST owners and operators should use EPA's TCLP test (see Table 7.1 and Table 7.2) to determine whether RCRA standards are relevant and appropriate in handling, treatment, storage, or disposal of such petroleum wastes.